Use of tetrameric cubane aggregates of lithium aryloxides as secondary building units in controlling network assembly†

Dugald J. MacDougall, J. Jacob Morris, Bruce C. Noll and Kenneth W. Henderson*

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Pre-aggregation of lithium aryloxides into tetrahedral arrangements followed by crystallization with the divergent Lewis base dioxane results in the preparation of three types of coordination polymers: zig-zag chains, (6,3) sheets, and diamondoid lattices.

The development of rational synthetic routes for the construction of structurally well-defined solids remains a major challenge for synthetic chemists.[1] The intense interest in this field can also be attributed to the potential use of designed materials in a wide variety of technologically important applications.[2] An emerging approach in the rational assembly of networks is through the use of secondary building units (SBUs), which are most commonly metal-containing aggregates that dictate the direction of polymer extension.[3] The use of SBUs is attractive in part because of their steric requirements and rigidity, which dramatically reduce the number of possible network topologies arising for a given node/linker combination.[4] Application of the SBU concept has mainly focused on inorganic solid-state chemistry and also on covalently linked transition metal cage complexes.[4,5] We became attracted towards the possibility of using *s*-block molecular aggregates to control the assembly of open-framework materials for use as novel solid-state reagents.[6] Although various types of coordination polymers containing *s*-block metals have previously been characterized, they have usually been prepared either inadvertently or to study localized metrical information.[7] Also, the majority of these polymers are composed of metals that can be considered as 'isolated' rather than part of a recognizable pre-organized aggregate. In these instances, the highly ionic nature of the *s*-block cations leads to effectively spherical nodes and consequently little control over the specific type of polymer produced. We believed that these issues could be overcome through the judicious choice of *s*-block SBU and divergent Lewis base linker. We targeted the formation of diamondoid networks through the use of tetrasolvated Li_4O_4 cubanes formed by lithium aryloxides. These complexes are excellent SBU candidates since they contain strong Li–O bonding, the metals are held in an approximately tetrahedral arrangement with one coordination site available for ligation, and there is a wide range of substituted phenols available for systematic studies.[8] The didentate donor dioxane was selected as Lewis base due to its capacity to act as a linear linker, its rigidity and its inability to chelate a lithium center.[9]

An exploratory molecular modeling study was conducted to determine the feasibility of dioxane acting as a bridging ligand between a pair of Li_4O_4 cubanes, since this structural pattern had not previously been characterized.[9] *Ab initio* geometry optimization calculations (HF/6-31G*) were conducted on lithium phenoxide cubanes solvated by dioxane to ensure an accurate portrayal of steric and electronic effects. These studies indicated that no notable energy penalty (<0.01 kcal mol^{-1}) is incurred on bridging a pair of tetrasolvated cubanes by dioxane.[10] This key result was confirmed by single-point density functional theory calculations (B3LYP/6-311G**, <0.04 kcal mol^{-1}) and established the viability of polymer formation.[11]

Suitable lithium aryloxides were then chosen based on their predilection to form tetrasolvated Li_4O_4 cubanes in the presence of monodentate Lewis bases.[8] Specific structural variants of these ligands were then selected as our understanding of these systems evolved. In this communication we outline the characterization of the three representative complexes $[\{(ROLi)_4.(dioxane)_x\}_\infty]$, R = Ph, $x = 3$ (**1**); R = 4-Et-C_6H_4, $x = 2.5$ (**2**); and R = 1-naphth, $x = 2$ (**3**), which typify our findings. Each complex was readily prepared by the direct deprotonation of the phenols in dioxane using BuLi as base, followed by crystallization (all first batch crystalline yields >50%). The results of the single crystal X-ray diffraction (XRD) studies‡ are detailed in Fig. 1 and illustrate the successful union of the tetrameric cubane Li_4O_4 SBUs with dioxane in assembling an unprecedented systematic series of *s*-block metal coordination polymers.[7] Powder XRD studies were compared with the theoretical patterns generated from the single-crystal data to confirm the homogeneity of the bulk samples.

Complex **1** forms a 1D polymer where individual Li_4O_4 cubanes link to a pair of neighbors through dioxane to give a zig-zag chain motif. Additionally, the lithium centers not involved in polymer extension are each bound to a terminal donor molecule, resulting in all the metals being tetracoordinate. Overall, the individual lithiated SBUs act as V-shaped nodes, with two of the four possible metal centers within the tetramers acting as points of polymer extension. In comparison, **2** adopts a more complex (6,3) 2D network architecture. The Li_4O_4 cubanes now utilize three of the four available lithium centers for bridging, resulting in effectively trigonal SBUs which self-assemble to form hexagonal sheets. Each individual hexameric macrocycle adopts a chair conformation with a cross-sectional diameter of $\approx$17–19 Å.[12] An intriguing discovery was the encapsulation of two dioxane guest molecules *within* each of the host hexameric rings. These guests lie in the cavity created by macrocycles and are capped at the top and bottom by the aryl groups. The final structural type is the targeted 3D cubic diamondoid lattice adopted by **3**. As originally desired, all four lithium centers of the cubanes act as points of polymer extension and the tetrahedral SBUs link to create a

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† Electronic Supplementary Information (ESI) available: crystallographic, experimental and computational data are available. See http://www.rsc.org/suppdata/cc/b4/b413434f/

*khenders@nd.edu

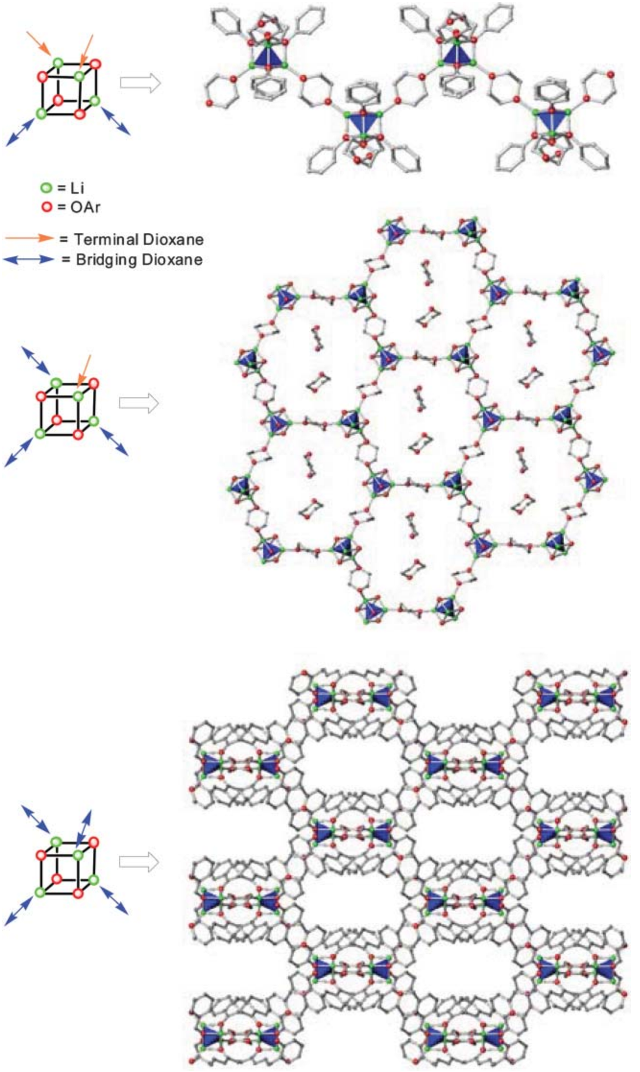

Fig. 1 Sections of the polymeric structures of: **1** (top) showing the 1D zig-zag chain motif; **2** (middle) depicting only the framework atoms of the (6,3) network and the two guest solvent molecules within each macrocycle; and **3** (bottom) showing the rectangular channels of the 3D diamondoid network created by the interlocking naphthyl units (enclatherated molecules are removed for clarity). Blue tetrahedra represent the positions of the four lithium centers within each cubane.

non-interpenetrated framework. Instead of the capped cavities found in **2**, complex **3** has large rectangular channels of 5.0 × 9.5 Å running throughout the solid.[12] In turn, these channels are filled with three enclatherated guest dioxanes per Li_4O_4 tetrameric unit.

The type of polymer formed can be rationalized in terms of balancing entropic factors with the efficient filling of space. Although our calculations indicate that bridging by dioxane is thermoneutral, there will be a substantial increase in entropy associated with polymer formation due to the gain in translational freedom of the liberated solvent molecules.[8a] Clearly, there will be an optimum length for the rigid anionic ligands of the SBUs in order to efficiently fill the hexameric macrocycles of the 2D sheets. If the ligands are too short this will result in energetically unfavorable large voids at the center of the rings, and conversely, if the ligands are too long the 2D arrangement will be destabilized by transannular interactions.[13] This analysis is consistent with the 1D chain structure observed for **1**, which carries the small PhO^- anions. Extension of the ligand at the *para*-position partially circumvents this problem and the longer 4-Et-$C_6H_4O^-$ anions, in combination with the guest dioxanes, fill the hexameric macrocycles with reasonable efficiency.[13] However, examination of the extended crystal-packing diagram of **2** shows interdigitation between neighboring 2D layers, suggesting that significant space still remains within the sheet. In order for a diamondoid structure to be formed it is necessary to occupy 3D adamantanoid cavities. This proves possible for **3** by lateral extension to the aromatic ring, which leads to excellent localized space filling in the 'corners' of the adamantanoids by interlocking of the naphthyl units. Space filling by interpenetration is precluded due to the (1-naphthylOLi)$_4$ cubanes being ≈14.2 Å in diameter whereas the adamantanoid cavities have dimensions of only 7.3 × 7.6 × 16.6 Å.[12] Moreover, the open structure found for **3** supports the conjecture that the use of robust SBUs in network assembly should promote the formation of porous materials.[3]

Our preliminary investigations indicate that the guest molecules within **3** can be removed *in vacuo* without disruption to the framework. Solvent loss was monitored by ^1H NMR spectroscopy through complete dissolution of samples in d_6-DMSO, followed by integration of the anion and dioxane signals. Initially, three enclatherated solvent molecules per Li_4O_4 unit are present but after 24 hours of evacuation (0.01 mmHg and 30 °C) the non-framework dioxane is competely removed. Comparison of the calculated, as prepared, and evacuated powder XRD patterns of **3** show only minor variations, demonstrating that the integrity of the framework is maintained. In addition, the macroscopic morphology of the crystals is retained on evacuation (perfect octahedra) allowing determination of the unit cell parameters by single-crystal XRD, and these also match those of the original material. Calculations indicate that 34.8% of the total volume within the crystal is potential solvent space.[14]

We are presently probing the generality of our rationalization for the type of polymer produced and have found that the dioxane complexes of 4-Me-C_6H_4OLi, 4-F-C_6H_4OLi and 4-Cl-C_6H_4OLi form 1D chains; 4-^iPr-C_6H_4OLi and 4-MeO-C_6H_4OLi form 2D (6,3) nets, and 2,4,6-Me_3-C_6H_2OLi forms an open 3D diamondoid framework. These results are entirely consistent with our proposals and will be discussed in detail elsewhere. Furthermore, our findings indicate that the new classes of readily assembled 2D and 3D periodic networks have significant potential in host–guest and open-framework chemistry and we are investigating the use of receptor sites built onto the ligand backbones to selectively capture guest molecules in their well-defined cavities. Finally, our demonstration of the successful use of *s*-block SBUs in the rational design of robust framework assemblies opens up a wide variety of readily available aggregate types (dimers, trimers, tetramers, hexamers, *etc.*), anionic partners (organyls, alkoxides, amides, halides, *etc.*) as well as divergent Lewis base linkers for further study.

Dugald J. MacDougall, J. Jacob Morris, Bruce C. Noll and Kenneth W. Henderson*
Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, 46556, USA. E-mail: khenders@nd.edu; Fax: +1-574-631-6652; Tel: +1-574-631-8025

Notes and references

‡ Crystallographic data for **1**: $C_{18}H_{22}Li_2O_5$, *M* 332.24, monoclinic, space group *C*2/*c*, $a = 13.0937(9)$, $b = 17.7646(12)$, $c = 15.7526(11)$ Å, $\alpha = 90$, $\beta = 94.853(4)$, $\gamma = 90°$, $V = 3651.0(4)$ Å^3, $Z = 8$, $T = 100(2)$ K, $\mu = 0.085$ mm^{-1}, R_1 ($I>2\sigma I$) 0.0411. **2**: $C_{92}H_{128}Li_8O_{22}$, *M* 1641.46, triclinic, space group $P\bar{1}$, $a = 14.3172(3)$, $b = 15.2696(3)$, $c = 24.5935(6)$ Å, $\alpha = 74.194(1)$, $\beta = 84.994(1)$, $\gamma = 62.507(1)°$, $V = 4584.39(17)$ Å^3, $Z = 2$, $T = 100(2)$ K, $\mu = 0.082$ mm^{-1}, R_1 ($I>2\sigma I$) 0.0575. **3**: $C_{15}H_{17}LiO_{3.5}$, *M* 260.23, tetragonal, space group *I*4(1)/*a*, $a = 15.0031(1)$, $b = 15.0031(1)$, $c = 24.7185(4)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 5563.96(10)$ Å^3, $Z = 16$, $T = 100(2)$ K, $\mu = 0.086$ mm^{-1}, R_1 ($I>2\sigma I$) 0.0458. CCDC 239838, 239840 and 239844. See http://www.rsc.org/suppdata/cc/b4/b413434f/ for crystallographic data in .cif or other electronic format.

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